

Sorption of Atrazine and Dicamba in Delaware Coastal Plain Soils: a Comparison of Soil Thin Layer and Batch Equilibrium Results

Richard M. Johnson^{1*} & J. Thomas Sims²

¹ USDA-ARS-SRRC, PO Box 19687, New Orleans, LA 70179 USA

² Department of Plant and Soil Sciences, College of Agricultural Sciences, University of Delaware, Newark, DE 19717 USA

(Received 1 May 1997; revised version received 24 April 1998; accepted 4 June 1998)

Abstract: The mobility and retention of atrazine and dicamba in six Atlantic Coastal Plain soils were estimated by soil thin-layer chromatography (soil-TLC). The soils studied were representative of the major agricultural regions in Delaware and were sampled, by horizon, to the water table. Four horizons from each profile were leached simultaneously with distilled water on one soil-TLC plate. Two values were obtained from each plate: the ratio of the distance traveled by the herbicide center of mass over that traveled by the solvent front (R_m), and a sorption distribution coefficient (K_d). The R_m values ranged from 0.06 to 0.94 for atrazine and from 0.80 to 0.94 for dicamba. Herbicide mobility was found to be greatest in coarse-textured soil horizons that contained low levels of organic matter, clay, and Fe and Al oxides. Correlation analysis indicated that effective cation exchange capacity, exchangeable acidity, exchangeable aluminum, and clay were useful predictive variables or both atrazine mobility and sorption. Organic matter was not useful for predicting soil-TLC derived sorption estimates; however, it was correlated to K_d -batch estimates. Distribution coefficients calculated from soil-TLC data were found to be in general agreement with K_d values obtained for the same soils by batch equilibrium techniques. The average K_d -soil-TLC values for atrazine and dicamba were $2.09 (\pm 2.24)$ and $0.03 (\pm 0.02)$, respectively. The ratio of the batch K_d to the soil-TLC K_d ranged from 0.1 to 19 ($\bar{x} = 1.6$, $SD = 3.8$) for atrazine and from 2.9 to 38 ($\bar{x} = 12.6$, $SD = 8.7$) for dicamba. Thus, although for some horizons agreement between the two methods was good, for other horizons significant discrepancies existed. It is suggested that the soil-TLC gives results under non-equilibrium conditions, whereas the batch procedure is, by definition, at quasi-equilibrium. These fundamental differences may account for the observed differences between the two methods. It is also suggested that, due to this difference, the soil-TLC procedure can provide additional information relevant to herbicide partitioning in the field environment that is not provided by traditional batch equilibrium techniques. © 1998 Society of Chemical Industry

Pestic. Sci., **54**, 91–98 (1998)

Key words: herbicide mobility; herbicide leaching; herbicide sorption; non-equilibrium sorption; soil properties

1 INTRODUCTION

Bailey and White¹ stated that sorption by soil is one of the most important reactions determining the extent of herbicide transport in the soil environment. Sorption

determines the quantity of herbicide in the soil solution and, thus, the amount that is available to be leached; thus herbicide mobility would be inversely correlated with those soil properties that are positively correlated with sorption. Atrazine mobility would be expected to correlate with the effective cation exchange capacity in low pH soils, and with organic matter at all pH values.

* To whom correspondence should be addressed.

Also, because of the acidity of the soil surfaces, protonation would be expected to begin, and increase with decreasing pH, at pH values above but near the pK_a of 1.68.^{2,3} Soil properties associated with anion sorption, such as total and amorphous Fe and Al oxide content and anion exchange capacity would be expected to correlate with dicamba sorption. Dicamba is a weakly acidic compound that will exist primarily as an anion at pH values greater than its pK_a of 1.93.⁴

Soil thin-layer chromatography (soil-TLC) was developed by Helling and Turner⁵ as a technique for evaluating pesticide mobility. Helling⁶ has used the R_f values (the ratio of the distance traveled by the solute front to that of the solvent front) on a standard soil, a Hagerstown silty clay loam, to classify pesticides into five mobility classes from very mobile to immobile. Helling⁷ compared the mobilities of 13 pesticides on 14 soils. The mobility classification for atrazine varied from 'low' to 'mobile' ($R_f = 0.35-0.89$) for different soils. The range in R_f values for 2,4-D was 0.41 to 1.00, 'intermediate' to 'very mobile'. Investigating this effect further, Helling⁷ utilized multiple regression analysis between R_f values and selected soil properties. The results indicated that mobility of non-ionic compounds was directly related to water flux and inversely related to sorption of similar compounds, field moisture capacity, organic matter, clay content and CEC. Mobility of acidic compounds was directly related to water flux and pH.

Recently, Arienzo *et al.*⁸ used soil-TLC to relate soil properties to the mobility of diazinon, and Sánchez-Camazano *et al.*⁹ used soil-TLC to evaluate the soil mobility of ethofumesate. Several other researchers have also attempted to extend soil-TLC methodology. Sánchez-Martín *et al.*¹⁰ used a linear ¹⁴C analyzer to quantify the results from soil-TLC experiments. This instrument reads the radioactivity present on the soil-TLC plate in a fashion similar to UV densitometers. The authors reported that the linear analyzer was a non-destructive technique that yielded results comparable to traditional autoradiography techniques. The linear analyzer also enabled determination of the R_f at the point of maximum pesticide concentration, in addition to producing a more quantitative evaluation of the relative distribution of the herbicide on the soil-TLC plate. Finally, Mojašević and Helling¹¹ described a method that used multi-residue gas chromatography to analyze developed soil-TLC plates. This procedure permitted the analysis of the relative mobilities of seven pesticides that were co-applied in one spot and also agreed with results obtained by autoradiography.

The mobility of a herbicide in a given soil is influenced by many chemical and physical properties of the soil and herbicide in question. In addition, the method used to determine mobility may influence the predicted mobility. The objectives of the present experiments were: (1) to determine the relative mobilities of atrazine and dicamba in six Delaware Coastal Plain soil profiles;

(2) to investigate the relationship between selected soil properties and herbicide mobility and retention as determined by soil-TLC; and (3) to evaluate soil-TLC as a method for determining distribution coefficients of herbicides.

2 MATERIALS AND METHODS

2.1 Soils and herbicides

The soils used in this study have been described previously.¹² Briefly, the soils investigated were representative of the major agricultural regions of the state of Delaware, and included three Ultisols, one Inceptisol, one Entisol and one Alfisol. Differences in herbicide mobility between these soils and horizons were expected, because of significant variation in those chemical and physical properties associated with herbicide sorption. Selected chemical and physical properties are presented in Table 1. Details of these properties and their determination have been described previously.¹² The herbicides used in these studies were atrazine (6-chloro-*N*²-ethyl-*N*⁴-isopropyl-1,3,5-triazine-2,4-diamine) and dicamba (2-methoxy-3,6-dichlorobenzoic acid). These herbicides are used extensively in grain production systems in the Atlantic Coastal Plain.

2.2 Soil thin layer chromatography

Soil-TLC plates were prepared according to the procedure of Helling and Turner.⁵ All soil was air-dried and passed through a 1-mm sieve to aid in uniformity of the soil layer. Helling⁶ found that sieving the soil to this size did not significantly affect herbicide mobility on the soil-TLC plate, as compared to the un-sieved soil. The soil was then slurried and applied to 25 × 25 cm Plexiglas plates. The exact weight of soil applied (~25 g) and the moisture weight fraction (θ_m) of the slurry were also determined so that the bulk density (ρ_b) and total porosity (f) of the soil layer could be determined. Bulk density was determined by calculating the oven-dry weight of the soil applied to the plate (oven-dry weight = wet weight/(1 + θ_m)) and then applying the relation $\rho_b = \text{oven-dry weight}/\text{volume}$ (note that the volume was calculated from the dimensions of the soil layer). Porosity was calculated by the relation $f = (1 - (\rho_b/\rho_s))$, where ρ_s = particle density. Particle density was assumed to be 2.65 g cm⁻³. Soil from four horizons could be applied to a single plate. The individual lanes were 5 cm wide and 25 cm long. The thickness of the soil layer was controlled by applying layers of tape between soil lanes. The number of layers of tape neces-

TABLE 1
Physical and Chemical Properties^a of the Surface and Subsoil Horizons of Six Delaware Soils

<i>Soil</i>	<i>Horizon</i>	<i>Depth (cm)</i>	<i>OM^a</i> (%)	<i>Sand</i> (%)	<i>Silt</i> (%)	<i>Clay</i> (%)	<i>pH</i>	<i>ECEC</i> (<i>cmol kg⁻¹</i>)	<i>HM</i> (%)	<i>ACID</i> (<i>cmol kg⁻¹</i>)	<i>EXAL</i> (<i>cmol kg⁻¹</i>)	<i>AMFE</i> (<i>g kg⁻¹</i>)	<i>AMAL</i> (<i>g kg⁻¹</i>)
Evesboro s	Ap	0–33	1.0	94	5	1	6.4	0.50	0.20	0.48	0.23	0.03	0.04
	C1	33–79	0.1	92	7	1	4.7	0.30	0.17	0.30	0.16	0.02	0.03
	C2	79–135	0.1	97	2	1	4.6	0.40	0.27	0.35	0.22	0.02	0.03
	2C4	170–232	0.1	89	6	5	5.0	0.40	0.20	0.41	0.27	0.02	0.05
Evesboro ls	Ap	0–23	1.0	85	12	3	6.1	0.10	0.21	0.13	0.02	0.04	0.06
	E1	23–51	0.2	87	10	3	5.6	0.20	0.27	0.16	0.04	0.01	0.02
	E2	51–91	0.1	96	2	2	5.7	0.03	0.10	0.03	nd	0.02	0.02
	Bt1	91–112	0.1	83	2	15	5.0	0.80	0.04	0.76	0.57	0.07	0.08
Kalmia ls	A	0–18	2.8	75	18	7	6.1	2.60	0.72	2.6	1.9	0.08	0.10
	E	18–48	0.4	75	19	6	4.2	1.10	0.49	1.1	0.8	0.03	0.06
	Bt	48–81	0.2	68	18	14	4.3	2.40	0.09	2.4	2.0	0.06	0.09
	C1	107–135	0.1	79	7	14	4.5	1.60	0.04	1.6	1.3	0.02	0.07
Osier sl	A	0–23	2.5	72	18	10	5.8	1.90	0.57	1.88	1.48	0.09	0.20
	Bg1	23–46	0.3	82	11	7	4.8	0.90	0.33	0.88	0.68	0.03	0.11
	Bg2	46–76	0.1	83	9	8	4.9	1.10	0.03	1.11	0.90	0.05	0.08
	2Cg	76–137	0.1	77	7	16	4.5	1.40	0.10	1.44	1.18	0.01	0.06
Sassafras sl	Ap	0–23	1.1	67	26	7	5.8	0.40	0.26	0.43	0.26	0.07	0.11
	Bt	23–66	0.2	72	9	20	5.5	0.04	0.07	0.04	nd	0.09	0.10
	C1	66–107	0.1	82	7	11	5.9	0.01	0.05	0.01	nd	0.06	0.08
	C2	107–203	0.1	86	6	7	6.0	0.01	0.04	nd	nd	0.06	0.07
Matapeake sil	Ap	0–25	1.7	9	75	16	5.9	0.30	0.43	0.68	0.33	0.28	0.18
	Bt	25–69	0.3	6	75	16	5.6	0.03	0.07	0.11	0.03	0.55	0.16
	2C1	69–84	0.1	85	8	7	5.5	0.01	0.11	0.05	nd	0.21	0.06
	2C2	84–97	0.1	94	3	3	5.5	0.01	0.13	0.06	nd	0.25	0.11

^a OM = organic matter, ECEC = effective cation exchange capacity, HM = humic matter, ACID = exchangeable acidity, EXAL = exchangeable aluminum, AMFE = amorphous iron, AMAL = amorphous aluminum.

sary to achieve a 1-mm layer was determined by a micrometer. Soil layers were smoothed to the desired thickness with a glass rod. The soil-TLC plates were prepared in duplicate and allowed to dry overnight. Ten μl of [^{14}C]atrazine and [^{14}C]dicamba (22 200 dpm) were applied to each soil horizon 2 cm from the bottom of the plate and allowed to dry. The plates were then placed in a tank of deionized water and allowed to develop 10 cm from the spotting origin, or 12 cm from the bottom of the plate. Helling⁶ did not find a significant difference in R_f values between plates developed with deionized water and those developed with 0.01 M CaCl_2 . The exact position of each solvent front was marked directly on the plate. The soil plates were scraped at 1-cm intervals, to determine herbicide position. The scraped soil was then placed directly in 15 ml of scintillation fluid (ScintiverseTM E, Fisher Scientific) and counted for three replications of 10 min on a Searle Isocap/300 liquid scintillation spectrophotometer.

2.3 Statistics

Several researchers have attempted to relate soil-TLC mobility results to pesticide sorption. Using the theory of Martin and Synge,¹³ one may derive a relation between the R_m and K_d values of a particular herbicide, where,

$$R_m = \frac{\text{distance traveled by concentration maxima}}{\text{distance traveled by solvent front}} \quad (1)$$

$$K_d = (A_s/A_m)[(1/R_m) - 1] \quad (2)$$

where

A_s = cross-sectional area of the stationary phase.

A_m = cross-sectional area of the mobile phase.

Rhodes *et al.*¹⁴ used linear regression to relate R_f values from soil-TLC studies to Freundlich sorption K values from batch studies for five pesticides on a Keyport silt loam. Graphical presentation indicated a good agreement, although coefficients of determination were not reported. The empirical relation developed was:

$$K = [(1/R_f) - 1] + 0.85 \quad (3)$$

The relation of Martin and Synge¹³ was extended by Hamaker¹⁵ to include a term relating the soil pore volume to the cross-sectional area of the liquid phase in a saturated soil. This relation is:

$$R_m = \frac{1}{1 + K_d(d_s)(1/\Phi^{2/3} - 1)} \quad (4)$$

where

d_s = particle density.

Φ = soil pore fraction.

Using this relation, Hamaker¹⁵ predicted soil-TLC R_f values for 17 pesticides, originally determined by Helling and Turner⁵ and Helling⁶, with an average deviation of $0.4(\pm 0.27)$. The author indicated that some of the observed disparities may be explained by the fact that the calculated values represent R_m values, where the measured values are R_f values.

In our study, the R_m values were used as an index of herbicide mobility and to obtain an estimate of the herbicide-soil distribution coefficient. They were determined by first fitting the soil-TLC plate concentration profile to cubic spline equations (Ref. 16, PROC IML). These data were then used to determine the position of maximum herbicide concentration on the soil plate. Equations (1) and (4) were then used to calculate R_m and K_d values, respectively. Distribution coefficients determined by this procedure were compared to those determined by batch techniques.¹² Correlation analyses (Ref. 16, PROC CORR) were performed between sorption and mobility estimates and soil properties. To enable a more complete analysis of the relation between herbicide sorption and mobility, the present data set for atrazine was combined with atrazine soil-TLC and batch sorption data from a previous study.¹⁷ This increased the number of soils from 6 to 10 and the number of horizons from 24 to 46. Two separate analyses were performed on the combined data set. Initially, all horizons were included in the analysis to investigate the overall influence of the soil properties investigated on atrazine mobility and sorption. The surface horizons of each soil were then excluded and correlations were re-calculated to investigate the influence of subsoil properties on mobility and sorption.

3 RESULTS AND DISCUSSION

3.1 Herbicide mobility

The mobilities of atrazine and dicamba were distinctly different. The R_m values for atrazine ranged from 0.06 to 0.94, while the values for dicamba ranged from 0.80 to 0.94 (Table 2). These data compare well with those of Helling⁷ for both dicamba ($R_f = 0.96$) and atrazine ($R_f = 0.47$). The large range in atrazine R_m values is not surprising considering the number of different soils investigated. It should also be noted that distinct tailing of atrazine was noticed on virtually all soil-TLC plates, an effect also observed by Helling.⁶ Tailing of the herbicide retards the progress of the solute center of mass (R_m), until it lags significantly behind the solute front (R_f). When tailing does not occur the R_m value would be expected to be closer to the R_f value. This behavior

TABLE 2
Atrazine and Dicamba R_m , K_d -TLC and K_d -Batch Values for Surface and Subsoil Horizons of Six Delaware Soils

Soil	Horizon	Atrazine			Dicamba		
		R_m	K_d -TLC (l kg ⁻¹)	K_d -Batch (l kg ⁻¹)	R_m	K_d -TLC (l kg ⁻¹)	K_d -Batch (l kg ⁻¹)
Evesboro s	Ap	0.14	1.56	0.64	0.94	0.02	0.09
	C1	0.23	0.84	0.30	0.94	0.02	0.19
	C2	0.94	0.02	0.38	0.94	0.02	0.27
	2C4	0.06	4.04	0.58	0.94	0.02	0.25
Evesboro ls	Ap	0.06	2.92	0.69	0.94	0.01	0.19
	E1	0.60	0.16	0.29	0.94	0.01	0.42
	E2	0.62	0.13	0.38	0.94	0.01	0.37
	Bt1	0.06	3.87	0.62	0.80	0.06	0.48
Kalmia ls	A	0.06	3.69	2.15	0.94	0.02	0.13
	E	0.36	0.43	0.14	0.94	0.02	0.13
	Bt	0.06	4.92	1.84	0.94	0.02	0.17
	C1	0.06	4.92	1.13	0.94	0.02	0.41
Osier sl	A	0.19	1.18	1.52	0.94	0.02	0.14
	Bg1	0.20	0.90	0.49	0.94	0.02	0.10
	Bg2	0.06	3.69	0.52	0.94	0.02	0.21
	2Cg	0.26	1.01	0.73	0.80	0.09	0.26
Sassafras sl	Ap	0.32	0.53	0.83	0.94	0.02	0.21
	Bt	0.19	1.38	0.73	0.80	0.08	0.25
	C1	0.43	0.40	0.52	0.94	0.02	0.36
	C2	0.44	0.35	0.51	0.94	0.02	0.48
Matapeake sil	Ap	0.23	1.77	2.01	0.94	0.03	0.18
	Bt	0.06	9.51	0.88	0.94	0.04	0.11
	2C1	0.22	1.15	0.49	0.94	0.02	0.29
	2C2	0.31	0.80	0.58	0.80	0.02	0.21

could result in the observed difference between R_m and R_f values. The large R_m value for dicamba would indicate that little or no sorption of the herbicide is occurring and that leaching could occur readily.

Clear differences in atrazine mobility were noted between the soils investigated. This contrasts with dicamba, which was highly mobile in all soils studied. Averaged across all horizons, the R_m values for atrazine were: 0.34, 0.34, 0.34, 0.20, 0.18 and 0.14 for the Sassafras sandy loam, Evesboro sand, Evesboro loamy sand, Matapeake silt loam, Osier sandy loam and Kalmia loamy sand soils respectively. This ranking closely followed increases in soil organic matter. The average organic matter contents, across horizon were 0.21, 0.35, 0.38, 0.54, 0.75 and 0.87% for the Evesboro sand, Evesboro loamy sand, Sassafras sandy loam, Matapeake silt loam, Osier sandy loam and Kalmia loamy sand soil respectively. Talbert and Fletchall¹⁸ reported a positive correlation between soil organic matter and atrazine sorption ($r = 0.82$) and Helling¹⁹ observed a negative correlation ($r = -0.656$) with atrazine mobility. In all soil profiles where a Bt horizon existed, a decrease in herbicide mobility occurred, compared to overlying or

underlying horizons. For example, R_m values for atrazine in the E horizon of the Kalmia loamy sand were 0.36, compared to 0.06 in the Bt horizon. In the Ap and Bt horizons of the Matapeake silt loam, the R_m value decreased from 0.23 to 0.06. These effects were also observed for dicamba. Note the decrease in mobility in the Bt horizon of the Sassafras sand loam, compared to the Ap horizon ($R_m = 0.80$ and 0.94), and the decrease in the Bt horizon of the Evesboro loamy sand, compared to the Ap, E1 and E2 horizons ($R_m = 0.80$, 0.94, 0.94 and 0.94). Results of this study suggest that organic matter and clay contents can have important effects on the mobility of atrazine and dicamba. Clays and oxides become more important in subsoils where there is insufficient organic matter to impede herbicide leaching.

3.2 Herbicide sorption

Averaged across all soil horizons, the K_d (litre kg⁻¹) values determined by soil-TLC were 2.09(± 2.24) and 0.03(± 0.02) for atrazine and dicamba respectively (Table 2). The average K_d (litre kg⁻¹) values determined

TABLE 3
Simple Correlation Coefficients between Atrazine Mobility and Distribution Coefficients and Selected Soil Properties from the Combined Data Set

Soil property	R_m^a	STLC- K_d^a (litre kg^{-1})	Batch- K_d^a (litre kg^{-1})
Sand	0.37**	-0.56***	-0.51***
Silt	-0.31*	0.44**	0.40**
Clay	-0.42**	0.62***	0.57***
pH	0.09	-0.27	-0.23
Organic matter	-0.31*	0.06	0.53***
Humic matter	-0.16	-0.05	0.42**
Effective cation exchange capacity	-0.52***	0.64***	0.67***
Exchangeable acidity	-0.37*	0.64***	0.59***
Exchangeable aluminum	-0.36*	0.62***	0.57***
Amorphous aluminum	-0.10	0.36*	0.37*
Amorphous iron	-0.04	0.21	-0.03
Batch- K_d	-0.63***	0.65***	—
STLC- K_d	-0.64***	—	0.65***
R_m	—	-0.64***	-0.63***

^a * $P_{.05}$, ** $P_{.01}$, *** $P_{.001}$

in batch sorption experiments for the same soil were 0.79 and 0.25 for atrazine and dicamba respectively.¹² The ratio of the batch K_d to the soil-TLC K_d ranged from 0.1 to 19 ($\bar{x} = 1.6$, $SD = 3.8$) for atrazine and from 2.9 to 38 ($\bar{x} = 12.6$, $SD = 8.7$) for dicamba. The large range in ratios indicates that, while for some horizons the agreement between the methods was good, for many horizons significant disparities existed. Correlation analysis indicated that the two methods were not significantly correlated for dicamba and only marginally for atrazine when all horizons were considered, $r = 0.14^{ns}$, and $r = 0.39$, $P = 0.06$, respectively. When the Bt horizon of the Matapeake soil was excluded from the analysis, the correlation for atrazine increased to $r = 0.51^*$, while the correlation for dicamba remained not significant. Slightly improved results were obtained in subsoils for atrazine, with $r = 0.50^*$, with the Matapeake Bt and $r = 0.59^*$ without this horizon.

The differences in K_d estimates (K_d -soil-TLC versus K_d -batch) most likely arise from fundamental differences in methodology. If one considers the batch estimate to represent the equilibrium value for sorption and desorption, then the soil-TLC procedure may represent non-equilibrium conditions that overestimate the K_d value for atrazine and underestimate the K_d value for dicamba. Rao *et al.*²⁰ have discussed two approaches to describing non-equilibrium sorption-desorption. The first approach assumes that physical processes are the source of non-equilibrium. The degree of sorption would be diffusion-limited and decrease with increasing pore-water velocity. The second approach assumes that chemical processes are the source of non-equilibrium. The chemical in question is readily sorbed, but desorption is retarded, resulting in a tailing of the chemical and an increase in apparent sorption.

In our study, both sources of non-equilibrium are suggested. In those horizons where atrazine is strongly sorbed, such as the Bt horizons of the Kalmia, Matapeake and Sassafras soils, the K_d estimate from soil-TLC is larger than the batch estimate, [$K_d = 4.92$, 9.51 and 1.38 compared to 1.84, 0.88 and 0.73 litre kg^{-1}]. In desorption experiments with the same soils, increasing clay content was associated with increases in apparent hysteresis.²¹ If an increase in hysteresis occurred in these horizons then the net result would be an increase in the predicted K_d value. In those horizons where atrazine is not strongly sorbed, and for all dicamba-horizon combinations, the soil-TLC K_d estimate is generally lower than the batch estimate. For example, consider atrazine sorption on the E, E1 and E2 horizons of the Kalmia and Evesboro loamy sand soils, $K_d = 0.43$, 0.16 and 0.13 litre kg^{-1} for the soil-TLC estimate compared to 1.14, 0.29 and 0.38 litre kg^{-1} for the batch estimate. These horizons are coarse-textured (>75% sand), and the time required to leach these horizons on the soil plate was significantly less than the Bt horizons (30 min compared to 4–5 h). It is therefore likely that reaction time between herbicide and soil on the soil-TLC plate was not adequate.

It is possible to calculate a water flux for the soil-TLC plates if one assumes saturated flow conditions. The flux for a typical E horizon, in this study, was 5 cm h^{-1} , and the flux for a Bt horizon was 0.63 cm h^{-1} . Davidson and Chang²² reported a significant increase in picloram sorption when the pore-water velocity was reduced from 5.8 to 0.59 cm h^{-1} . The authors attributed this observation to an increase in residence time available for equilibrium sorption at the lower pore water velocity. Thus it is likely that insufficient time was available in our study for equilibrium to

occur because of the higher flux present in the E horizons. All batch K_d estimates for dicamba sorption¹² were from 5 to 10 times greater than the corresponding soil-TLC estimate. Dicamba would be expected to exist as an anion at the pH levels of the soils in this study. Sites for anion sorption in the soil are generally associated with amorphous iron and aluminum oxides and soil organic matter. It is likely that sufficient time was not available for diffusion of the herbicide to these sites.

3.3 Correlation analysis of herbicide mobility

3.3.1 Atrazine mobility

The soil properties most highly correlated with R_m , were effective cation exchange capacity, clay and sand, with $r = -0.52^{***}$, -0.42^{**} , 0.37^{**} , respectively (Table 3). In subsoils (Table 4), the highest correlations were between atrazine mobility and effective cation exchange capacity, exchangeable acidity, exchangeable aluminum and clay ($r = -0.56^{***}$, -0.50^{**} , -0.49^{**} , -0.49^{**}). Organic matter was only marginally correlated with R_m with $r = -0.31^*$ for all soils and -0.44^{**} in subsoils, respectively (Tables 3, 4). These combined observations agree generally with those of Helling,¹⁸ who investigated the mobility of 12 pesticides on 14 surface soils. The author reported significant correlations between clay, CEC, organic matter and atrazine mobility ($r = -0.609^*$, -0.557^* , -0.656^*). The results also support previous observations¹² on the importance of exchangeable acidity to herbicide sorption and mobility. Exchangeable acidity appears to be an extremely useful predictive variable for herbicide sorption and mobility, particularly in subsoils. Numerous researchers have indicated that soil acidity plays an extremely important role in determining the retention and mobility of ionizable pesticides. Nicholls and

Evans^{3,4} studied the sorption of a number of these compounds in field soils. They reported that many herbicides (e.g. dicamba) are moderately polar, weak acids and would be present in the soil in the dissociated form. Sorption of these compounds would be slight in acid soils and even less in neutral and alkaline soils. Sorption of the weakly basic herbicides (i.e. atrazine) was found to increase with decreasing pH, due to increased protonation of the compound. At higher pH values, sorption decreased. Our data also suggest that exchangeable aluminum may also be a useful predictive variable and that organic matter appears to exert a rather insignificant effect on atrazine mobility. The relatively small effect of organic matter on atrazine mobility has been noted for other pesticides. Arienzo *et al.*⁸ reported that the mobility of diazinon was significantly correlated to organic matter in soils where organic matter was $>2\%$, but not correlated when organic matter was $<2\%$. Sánchez-Camazano *et al.*⁹ observed a weak correlation between organic matter and the R_f for ethofumesate ($r = -0.41$, $P < 0.1$).

3.3.2 Atrazine sorption

In the combined data set, atrazine K_d -soil-TLC estimates were significantly correlated with K_d -batch estimates ($r = 0.65^{***}$) (Table 3). Other soil properties that were highly correlated with K_d -soil-TLC values included effective cation exchange capacity, exchangeable acidity and aluminium, clay and sand, ($r = 0.64^{***}$, 0.64^{***} , 0.62^{***} , 0.62^{***} , -0.56^{***}). These observations were consistent with the R_m estimates, as these properties possessed significant negative, or positive in the case of sand, correlations with atrazine mobility. Marginal correlations were obtained for silt and amorphous aluminum, ($r = 0.44^{**}$, 0.36^*), the reverse trend observed for the mobility data (Table 3).

TABLE 4
Simple Correlation Coefficients between Atrazine Mobility and Distribution Coefficients and Selected Subsoil Properties from the Combined Data Set

Soil property	R_m^a	STLC- K_d (litre kg^{-1})	Batch- K_d (litre kg^{-1})
Sand	0.43**	-0.63***	-0.57***
Silt	-0.35*	0.54**	0.42**
Clay	-0.49**	0.65***	0.67***
pH	0.35*	-0.32	-0.59***
Organic matter	-0.44**	0.30	0.50**
Humic matter	0.09	-0.15	0.0003
Effective cation exchange capacity	-0.56***	0.74***	0.68***
Exchangeable acidity	-0.50**	0.68***	0.85***
Exchangeable aluminum	-0.49**	0.65***	0.83***
Amorphous aluminum	-0.05	0.43**	0.26
Amorphous iron	-0.04	0.23	-0.09
Batch- K_d	-0.64***	0.73***	—
STLC- K_d	-0.67***	—	0.73***
R_m	—	-0.67***	-0.64***

^a * $P_{.05}$, ** $P_{.01}$, *** $P_{.001}$.

For subsoils, the correlation between the K_d -soil-TLC and K_d -batch improved significantly ($r = 0.73^{***}$). An improvement was also observed for all soil properties that were correlated with the K_d -soil-TLC values, $r = 0.74^{***}$, 0.68^{***} , 0.65^{***} , 0.65^{***} , -0.63^{***} for effective cation exchange capacity, exchangeable acidity, exchangeable aluminum, clay and sand, respectively (Table 4).

At this point it is useful to compare the correlation coefficients obtained with soil-TLC to those for the standard batch-derived K_d values. In general the K_d -batch values were more strongly correlated with soil properties than were the K_d -soil-TLC values (Tables 3, 4). When all horizons were considered (Table 3), the correlations for effective cation exchange capacity, exchangeable acidity and aluminum, clay, organic matter and sand were $r = 0.67^{***}$, 0.59^{***} , 0.57^{***} , 0.57^{***} , 0.53^{***} , -0.51^{***} for the K_d -batch method. In subsoils, the correlations for all of these properties increased, particularly for exchangeable acidity and aluminum where $r = 0.85^{***}$ and 0.83^{***} , respectively. Perhaps the most significant difference in the correlation data for the two differently derived K_d values was for organic matter. When all horizons were included (Table 3), the correlation coefficient was 0.53^{***} and 0.06^{ns} between organic matter and the K_d -batch and K_d -soil-TLC, respectively. This decreased in subsoils, where the correlation coefficient for organic matter was 0.50^{**} for the K_d -batch and 0.30^{ns} for the K_d -soil-TLC (Table 4).

It is apparent that the K_d values derived by the two methods have some fundamental differences. The K_d -soil-TLC estimates appear to be more closely related to variables that are associated with easily accessible sorption sites (i.e. clay). The K_d -batch estimates, while related to these properties, are also associated with variables related to less accessible sorption sites (i.e. those present in soil organic matter). Sorption sites associated with organic matter may be less accessible in the soil-TLC system due to the greater time required for the herbicide to diffuse to the sorption sites within the organic matter matrix. Also the complex nature of the organic matter complex may result in exclusion of the herbicide from some sorption sites. The batch procedure, by definition, requires the system to be at quasi-equilibrium so that time would be sufficient for diffusion of the herbicide to occur. The K_d -soil-TLC is perhaps more realistic, considering that transport is involved; however, this assertion must be further tested.

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